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Potential Cause for Low Lead and Chromium Recoveries During Acid Extractions

Alan D. Hewitt and James H. Cragin

October 1992

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Abstract

When high concentrations (≥ 100 mg/L) of Pb and Cr (IV) are present together in solution, PbCrO_4 precipitates, resulting in losses of these two metals. Moderate acidification with 1–2% HNO_3 does not prevent precipitation loss. Caution is necessary when preparing standard solutions or handling acidic extracts of environmental samples containing high levels of Pb and Cr, since undetected formation of metal chromates will result in low recoveries of these metals.

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, *Metric Practice Guide*, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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**U.S. Army Corps
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Cold Regions Research &
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PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Geological Sciences Branch, and James H. Cragin, Research Chemist, Snow and Ice Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory.

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Potential Cause for Low Lead and Chromium Recoveries During Acid Extractions

ALAN D. HEWITT AND JAMES H. CRAGIN

INTRODUCTION

The most common techniques in use today for the determination of trace levels of pollutant metals in environmental samples are atomic absorption and atomic emission. Analytical interferences can be either instrumental or chemical. Many of the chemical interferences have been overcome by varying instrumental parameters, adding matrix modifiers or using optimal sample atomization techniques. However, chemical interferences causing elemental losses can also occur before analysis—e.g., incomplete sample dissolution or volatilization of compounds during sample treatment. Other than potential loss of Pb halides or the formation of sparingly soluble PbSO_4 , we found no mention in the literature of solution losses or even the compatibility of Pb and Cr when mixed metal standards from certified reference stock solutions are prepared.

Commercially, Cr is available in 1000 ppm (mg/L) certified reference stock solutions as $\text{K}_2\text{Cr}_2\text{O}_7$ or $[\text{NH}_4]_2\text{Cr}_2\text{O}_7$ in water. When introduced as the dichromate salt, the following species are present if the solution is aqueous or acidified with either HClO_4 or HNO_3 : CrO_4^{2-} , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and H_2CrO_4 (Cotton and Wilkinson 1988). If HCl is used for acidification, then the chlorochromate anion (CrO_3Cl^-) is the dominant species (Cotton and Wilkinson 1988). Thus, unlike many metals, chromium (VI) exists as anionic species in solution and, if present as chromate ion (CrO_4^{2-}), can cause losses of some heavy metal cations (i.e., Ba^{2+} , Pb^{2+} and Ag^+) by precipitation of insoluble chromates (Cotton and Wilkinson 1988). The absence of cau-

tion regarding such losses in common solution chemistry references (Katz and Jenniss 1983, Slavin 1984, Sulcek and Povondra 1989) is especially surprising for Pb, since the classical method for qualitative identification of the presence of this element is by precipitation of PbCrO_4 (Lyde 1961).

Recently, while doing quality assurance testing of a metal extraction procedure for soils using HNO_3 and a microwave oven, it was necessary to mix analytical reference standards containing 1000-mg/L concentrations of both Cr and Pb. Here, we describe problems encountered when mixing commercially available standards of these two metals; an analogous problem also may exist in the preparation of hazardous waste samples.

EXPERIMENTAL

The extraction procedure being evaluated in our study uses a 0.5-g soil subsample and 10 mL of concentrated HNO_3 sealed in a 120-mL Teflon vessel (Hewitt and Reynolds 1990). Dissolution is effected by heating in a microwave oven to temperatures approaching 120°C for approximately 13 minutes. Mixed metal standards for spiking were prepared from 1000-mg/L certified reference standards purchased from Fisher Scientific. As received, all of the reference standards other than Cr were acidified to 2 or 5% with HNO_3 . The chromium standard was prepared by dissolution of potassium dichromate in water. Aliquots of As, Cd, Cr, Cu, Pb and Zn were combined and taken to 100 mL with Type 1 water (Milli Q) to produce a concentrated standard spiking solution of pH 0.4

Table 1. Metal concentration ($\mu\text{g/L}$) determined in the diluted (1:400) mixed metal spiking solution.

	As	Cd	Cu	Cr	Pb
Expected	80.0	4.00	400	400	500
Measured	84.5	3.81	412	319	46.1
Percent recovered	106	95.2	103	79.8	9.22

containing 200 mg of Pb/L and 160 mg of Cr/L, from which a series of dilutions was subsequently made, as described in detail elsewhere (USATHAMA 1990). Concentrations of As, Cd, Cr, Cu and Pb in soil extracts and spiked quality assurance samples were determined by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) using a Perkin-Elmer Model 5100PC Zeeman atomic absorption spectrometer.

RESULTS AND DISCUSSION

Prior to the quality control spike and recovery test, we analyzed the stock spiking solution to verify that the metal concentrations were as expected (Table 1). On the basis of the procedure to be used for the spike recovery test, a 0.25-mL aliquot was removed from the mixed metal stock solution and diluted to 100 mL in a 10% HNO_3 solution (1:400 dilution). The concentrations of As, Cd and Cu were within $\pm 6\%$ of their expected values, but the recoveries both Pb and Cr were low at 9.2 and 80%, respectively, of the expected concentrations. Since Pb and Cr were lost in equimolar quantities, the low values were attributed to precipitation of PbCrO_4 .

We conducted two experiments to determine the upper concentration limits of Pb and Cr in typical mixed metal reference stock solutions, and to assess the effect of acidity on their loss from

solution. In the first experiment Pb and Cr were mixed in 2% HNO_3 in the following concentrations (mg/L)—2.0/1.6, 10/8, 20/16 and 100/80. These solutions sat overnight prior to dilution (1:400) and determination of Pb (Table 2). At concentrations of 20 mg/L and below, quantitative recoveries of Pb were obtained. At the 100 mg/L level, however, only 23% of the Pb was recovered.

In the second experiment the Pb and Cr concentrations were held constant and the acidity was varied. Thoroughly mixed solutions containing 200 mg/L of Pb and Cr were prepared in 1.0, 2.6, 5.0, 7.6 and 10% HNO_3 . Aliquots were withdrawn without further solution agitation after 1, 2, 3, 4, 6, 8, 10 and 14 days, diluted (1:400) and analyzed by GFAAS.

Figure 1 shows the percentage of the original 200 mg of Pb/L remaining in solution over a 2-week period. Overall, the higher the acid concentration, the higher the initial (1-day) and final (14-day) Pb concentrations. Lead precipitated as the chromate almost immediately from both the 1.0 and 2.6% acid solutions, while PbCrO_4 formation took hours and days for the 5.0 and 7.5% acid solutions respectively. No precipitate was observed in the 10% acid solution and Pb levels remained at the original 200 mg/L for the duration of the experiment (14 days), probably because of increased solubility of PbCrO_4 at this acidity. Unlike the 10% acid solution, the Pb concentration in all of the other acid solutions was not constant with

Table 2. Recoveries of mixed metal stock standards (mg/L) acidified with 2% HNO_3 .

Pb/Cr concentration	2.0/1.6	10/8	20/16	100/80
Measured Pb	2.01	10.5	20.4	23.0
Percent recovered	100	105	102	23

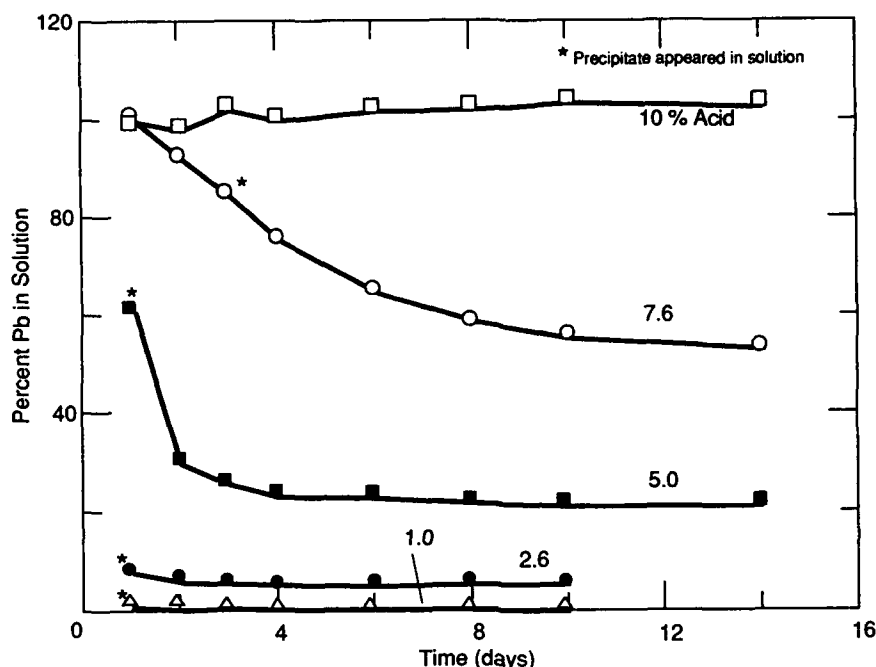


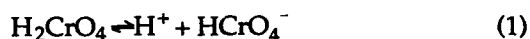
Figure 1. Percent of Pb (original concentration 200 mg/L) versus time in solutions of various acidity.

time. In 7.6% acid, the Pb concentration was still 200 mg/L after 1 day, then gradually decreased to about 54% (108 mg/L) of this value after 14 days. In 5.0% acid, the Pb concentration was 120 mg/L after 1 day, decreased to about 48 mg/L after 4–6 days, and thereafter remained stable. The 2.6% acid solution had a Pb concentration of 16 mg/L after 1 day, then decreased slightly and stabilized at 12 mg/L after 3 days. The 1% acid solution had a 2.9-mg/L Pb concentration on day 1, then decreased and stabilized at 2.0 mg/L thereafter.

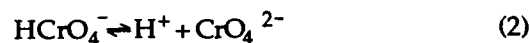
The above observations show that the final concentrations of Pb and Cr in concentrated solutions are controlled by not only acidity and solubility but by kinetics as well. For solutions containing 200 mg/L of Pb and Cr, acidification with HNO_3 in the range of 2–8% leads to kinetically slow (on the order of days) precipitation of these metals. The slow rate of precipitation is possibly caused by the low CrO_4^{2-} concentrations present in acidic solution, or the slow dissociation rate of H_2CrO_4 or HCrO_4^- , or both, to the chromate ion.

Acidity affects the chromium (CrO_4^{2-}) concentration, which in turn controls the Pb concentration. The equilibria and ionization constants (Lange

and Forker 1966) involved can be shown as follows (for simplicity we assume activities are unity)



$$K_1 = \frac{[\text{H}^+][\text{HCrO}_4^-]}{[\text{H}_2\text{CrO}_4]} = 1.8 \times 10^{-1}$$



$$K_2 = \frac{[\text{H}^+][\text{CrO}_4^{2-}]}{[\text{HCrO}_4^-]} = 3.2 \times 10^{-7}$$



$$K_{sp} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] = 1.77 \times 10^{-14}$$

The first two equations can be combined to give expressions for the fraction (α) of each chromium species that is present in solution at any given pH.

$$\alpha_{\text{H}_2\text{CrO}_4} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2} \quad (4)$$

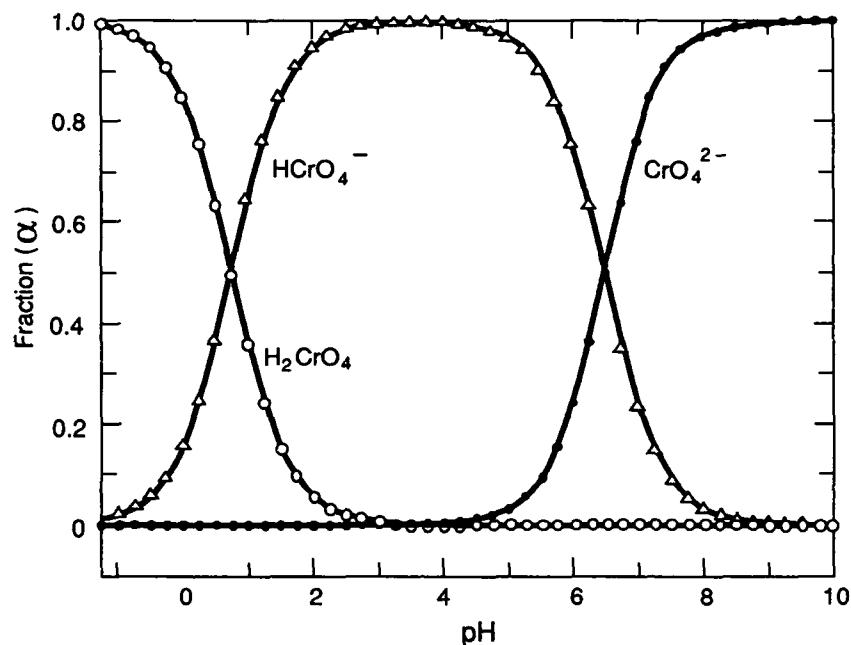


Figure 2. Fraction of chromium species versus pH.

$$\alpha_{\text{HCrO}_4^-} = \frac{K_1[\text{H}^+]}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2} \quad (5)$$

$$\alpha_{\text{CrO}_4^{2-}} = \frac{K_1 K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2} \quad (6)$$

Since the acid dissociation constants do not change, the only controlling variable is pH. From the pH and eq 4–6, we calculated the fraction of each chromium species present. A plot (Fig. 2) of this fraction vs pH shows that below pH 0.7 the predominant species is H_2CrO_4 , between pH 0.7 and 6.5 HCrO_4^- predominates, and above pH 6.5 CrO_4^{2-} is the major species. The pHs of acidified

solutions used in this study (Table 3) were all less than 0.8, so that the predominant chromium species in solution was H_2CrO_4 .

The equilibrium concentration of each chromium species can be found by multiplying the total initial chromium concentration by the fraction of that particular species present at a given acidity. For example, the concentration of chromate ion is

$$[\text{CrO}_4^{2-}] = [\text{Cr Total}] \alpha_{\text{CrO}_4^{2-}} \quad (7)$$

Since $\alpha_{\text{CrO}_4^{2-}}$ is given by eq 6 and Cr Total is 200 mg/L, solving for the chromate ion concentration in 1% (0.16 m/L) acid, we have

$$[\text{CrO}_4^{2-}] = (200 \text{ mg/L}) \quad (8)$$

$$\frac{(0.18) (3.2 \times 10^{-7})}{(0.16)^2 + (0.18) (0.16) + (0.18) (3.2 \times 10^{-7})}$$

$$[\text{CrO}_4^{2-}] = 2.1 \times 10^{-4} \text{ mg/L or } 2.1 \times 10^{-7} \text{ g/L} \quad (9)$$

Knowing the CrO_4^{2-} concentration, we can calculate the Pb^{2+} concentration from the solubility product

Table 3. Acid concentrations and pHs of solutions used to study the effect of acidity upon Pb losses.

Acid concentration (%)	pH	$[\text{H}^+]$ (mg/L)
1.0	0.80	0.16
2.6	0.39	0.41
5.0	0.097	0.79
7.6	-0.079	1.2
10.0	-0.20	1.6

$$[\text{Pb}^{2+}][\text{CrO}_4^{2-}] = 1.77 \times 10^{-14} \text{ mol}^2/\text{L}^2 \quad (10)$$

$$[\text{Pb}^{2+}] = \frac{1.77 \times 10^{-14} \text{ mol}^2/\text{L}^2}{1.8 \times 10^{-9} \text{ mol/L}} \quad (11)$$

$$= 9.8 \times 10^{-6} \text{ mol/L}$$

$$[\text{Pb}^{2+}] = 2.0 \text{ mg/L} \quad (12)$$

Thus, in the 1% (pH 0.8) acid solution, the theoretical equilibrium Pb concentration is 2.0 mg/L, in excellent agreement with the observed concentration (2.0 mg/L). Theoretical equilibrium Pb concentrations for other acidities were calculated simi-

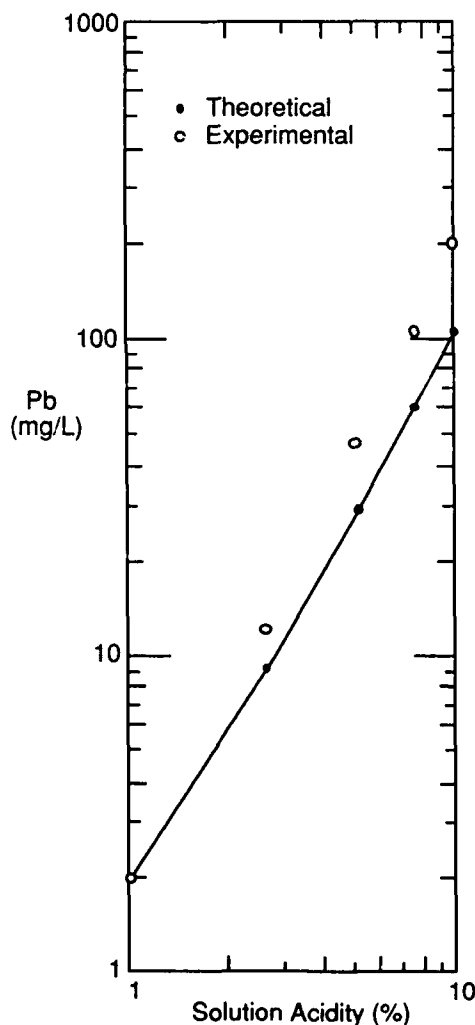


Figure 3. Theoretical and measured Pb concentrations versus acidity for solutions containing Pb and H_2CrO_4 .

larly and are plotted along with measured Pb concentrations versus solution acidity in Figure 3. Experimental Pb concentrations are 1.3 to 1.9 times greater than those calculated based upon H_2CrO_4 dissociation and PbCrO_4 solubility. This difference is probably due to the greater solubility (K_{sp}) of PbCrO_4 in acidic than in neutral solution. This contention is supported by the difference between the experimental and the theoretical Pb concentrations increasing with increasing acidity for the four most acidic solutions.

Our experiments only begin to show the complex equilibria that occur with chromium (VI) in solution, and further study is warranted of the kinetic effects of acidity, analyte concentrations above 200 mg/L, oxidation state of chromium in environmental samples and the precipitation of other potentially labile cations. The primary purpose of this report is to identify the problem for those researchers doing spike and recovery studies with mixed metal standards containing both Cr and Pb. However, similar precipitation losses are also likely during digestion of environmental samples. Particular attention should be paid to the dissolution and analysis of leaded paints, since PbCrO_4 is a common pigment. If high levels of Cr are present, HNO_3 extracts of soils from hazardous waste sites would show low recoveries of highly toxic Pb, resulting in undue complacency and possible inadequate remedial action.

SUMMARY

Mixed metal solutions of Pb and Cr (originally as dichromate), in the 100-mg/L concentration range, form a precipitate of PbCrO_4 , resulting in low recoveries of these two metals. Acidification with 10% HNO_3 will prevent precipitation at this concentration, as will a 2% HNO_3 acidification when the metal concentration is at least an order of magnitude less (10 mg/L). Sample treatment with Cr and Pb at the 100-mg/L level for recovery tests requires either the separate addition of Cr to the test matrix or the presence of high concentrations (about 10%, v/v) of acid in the mixed metal standard.

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